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"Imidazole and Its Derivatives as Inhibitors for Prevention of Corrosion of Copper"

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IMIDAZOLE AND ITS DERIVATIVES AS INHIBITORS FOR PREVENTION OF CORROSION OF COPPER

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ABSTRACT

The aim of this work was to investigate the efficiency of imidazole and its derivatives 4-methylimidazole, 4-methyl-5-hydroxymethylimidazole, 1-phenyl-4-methylimidazole, 1-(p-tolyl)-4-methylimidazole for corrosion inhibition of copper in 0.5M hydrochloric acid. Corrosion inhibition was studied using impedance spectroscopy and potentiodynamic methods. Results obtained from the AC impedance measurements are in good agreement with those obtained from d.c. polarisation measurements. The copper samples were also analysed by scanning electron microscopy (SEM) and X-rays microanalysis. These studies have shown that 1-(p-tolyl)-4-methylimidazole has the highest inhibitory efficiency.

Keywords: copper, hydrochloric acid, imidazoles, inhibition, EIS, SEM

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INTRODUCTION

Due to its good corrosion resistance, mechanical workability and excellent electrical and thermic conductivity, copper and its alloys are widely used in heating and cooling systems. Such systems are cleaned by acid pickling processes using HCl. It is important that the Cu-based system show corrosion resistance to the HCl. In such applications inhibitors are used to prevent copper dissolution and the destructive effect of HCl on the equipment.

Imidazole derivatives are well known corrosion inhibitors for metals and alloys¹⁻¹⁰. Imidazole is a heterocyclic organic compound with two nitrogen atoms forming part of a five-membered ring¹¹ (Figure 1). It is of particular importance as a corrosion inhibitor because it is environmentally friendly and has relatively low toxicity¹². In the present study the efficiency of a homologous series of imidazoles for inhibition of copper corrosion in 0.5M HCl was investigated. This series consisted of imidazole, 4-methylimidazole, 4-methyl-5-hydroxyimidazole, 1-phenyl-4-methylimidazole, 1-(p-tolyl)-4-methylimidazole (Figure 1).

Corrosion inhibition was investigated using AC impedance spectroscopy and potentiodynamic methods. The copper samples were also analysed by scanning electron microscopy (SEM) and X-rays microanalysis.

EXPERIMENTAL

Materials. Concentrated HCl (Merck), HNO₃ (Merck) and imidazole (Aldrich) were used as received. The inhibitors 4-methylimidazole, 4-methyl-5-hydroxymethylimidazole, 1-phenyl-4-methylimidazole and 1-(p-tolyl)-4-methylimidazole were obtained from Pliva pharmaceutical company (Zagreb, Croatia). Ethanol (Merck) and purified water (either doubly distilled or Millipore water) were used to rinse the samples and prepare solutions. The copper working electrode was of 99.98% purity. In addition, some studies were done on Cu composites consisting of two ~18 μm thick Cu films sandwiching an ~2 mm-thick film of epoxy resin. These Cu composites were obtained from Ericsson Nikola Tesla (Zagreb, Croatia).

Methods. Potentiodynamic experiments were conducted at 20°, 30°, 35° and 45 °C using a PARC 263A potentiostat/galvanostat controlled with PARC corrosion analysis software Model 352/252 SoftCorr™. A conventional three-electrode electrochemical cell of volume ~100 ml was used. The working electrode was prepared from a cylindrical copper rod insulated with polytetrafluoroethylene tape such that the area exposed to solution was 0.785 cm². A saturated calomel electrode (SCE) was used as the reference; a Pt plate electrode was used as the counter electrode. All potentials are reported vs SCE.

Prior to use the working electrode was etched for 30 sec in 7M HNO₃, rinsed in redistilled water and ethanol, and then used immediately¹³. The supporting electrolyte used for all studies was not deaerated 0.5M HCl. The investigated inhibitor was added to concentrations ranging from 1*10⁻⁴M to 0.15M, and the optimum concentration for each inhibitor was identified. The optimum concentration was determined experimentally by identifying the concentration of inhibitor that maximizes the inhibitory efficiency (z%). Data are reported here for this optimum concentration and for the concentration 0.01M. AC impedance measurements were conducted at 20 °C using an ACM Instruments impedance analysis system (Lancashire, England) and SpectroAnalyser software. An AC sinusoid of ±5 mV was applied at the corrosion potential; unless otherwise noted the frequency range 100 kHz to 0.02 Hz was employed. Instabilities in the impedance data were observed at lower frequencies. These instabilities were also observed when a PARC system was used to obtain analogues data. AC impedance data were obtained at 0.01M and at the optimum concentration. Scanning electron microscopy (SEM) was done on the copper composites. A Phillips SEM 505 microscope was used. The composites were HNO₃-etched and then immersed into 0.5M HCl, with and without addition of the desired inhibitor investigated (0.01M). The samples were immersed for 12 hours, rinsed with millipore water and ethanol and sputtered (Hummer 6.2, Anatech, Ltd) with gold (~5nm) to prevent charging in

the microscope. X-ray microanalysis data were obtained using a Kenex Microanalyst 8000.

RESULTS AND DISCUSSION

Tafel-Extrapolation Measurements. These measurements were done in the potential region ± 200 mV from the corrosion potential (E_{corr}), at a sweep rate of 0.166 mVs^{-1} . The corrosion potential was obtained by measuring the open-circuit potential as a function of time. Typical Tafel plots are shown in Figure 2. The corrosion current density j_{corr} was determined by extrapolating the Tafel lines. The corrosion efficiency (z) was calculated as follows:

$$z = \frac{100 \cdot (j_{\text{corr},0} - j_{\text{corr},i})}{j_{\text{corr},0}} \quad [1]$$

where $j_{\text{corr},0}$ and $j_{\text{corr},i}$ are the corrosion current densities in the uninhibited and inhibited solutions, respectively.

Table 1 shows the corrosion parameters (E_{corr} , the anodic and cathodic Tafel slopes (b_a and b_c), j_{corr} and protection degree, z) for the five inhibitors investigated at optimum concentrations and temperatures ranging from 20° to 45°C . These data show that the introduction of functional groups to the imidazole ring improves the inhibiting properties. The value of z increases in the following order: 4-methyl-5-hydroxymethylimidazole < 4-methylimidazole < imidazole < 1-phenyl-4-methylimidazole < 1-(p-tolyl)-4-methylimidazole. 1-(p-tolyl)-4-methylimidazole shows the best inhibiting efficiency at all

temperatures investigated. The best protection by 1-(p-tolyl)-4-methylimidazole is in the range of temperature between 30 to 35 °C. Figure 3 shows Tafel plots for copper in 0.5M hydrochloric acid to which was added 1-(p-tolyl)-4-methylimidazole at its optimum concentration (0.1M); data at four different temperatures are shown. In general, all inhibitors act as mixed inhibitors shifting E_{corr} to more negative values.

Linear Polarisation Measurements. These measurements were done over the potential region $E_{corr} \pm 15$ mV at a sweep rate of 0.166 mVs^{-1} . Typical linear-polarisation curves are shown in Figure 4. The polarisation resistance, R_p , was obtained from the slopes of such polarization curves. Figure 5 shows linear-polarization curves (at four different temperatures) for copper in a solution 0.5M in HCl and 0.01M in 1-(p-tolyl)-4-methylimidazole at different temperatures. The variation of inhibitory efficiency (η) with molecular structure is identical to that observed from the Tafel-extrapolation method. Finally, as clearly shown by the lower slope in Figure 4, these measurements confirm that 1-(p-tolyl)-4-methylimidazole is the best inhibitor.

AC - Impedance Measurements. Figure 6 shows Nyquist plots for all inhibitors at their optimum concentrations. The polarisation resistance is given by¹⁴

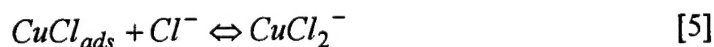
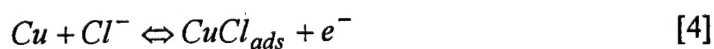
$$R_p = \lim_{\omega \rightarrow 0} \text{Re}\{Z_f\}_{E=E_{corr}} \quad [3]$$

where $\text{Re}\{Z_f\}$ represents the real part of the complex faradaic impedance Z_f and ω corresponds to the angular velocity of the AC signal ($\omega=2\pi f$, where f is frequency, Hz). The R_p values were obtained by fitting the experimental Nyquist data to a simple semicircle and extrapolating to $Z(\text{im})=0$. The effect of molecule structure on the inhibitory efficiency is the same as was observed for the other two electrochemical methods. Hence, these three very different methods are telling a consistent story about the efficacy of these molecules for inhibition of copper corrosion.

Scanning Electron Microscopy. Figure 7 shows scanning electron microscopic images of a copper composite sample after immersion in 0.5M HCl without inhibitor for 12 hours. Figure 8 shows analogous images for a sample that had been immersed in a solution 0.5M in HCl and 0.01M in 1-(p-tolyl)-4-methylimidazole. Looking first at the low magnification images (Figure 7B and 8B) we see that the surface that had not been exposed to the inhibitor solution shows crystalline deposits; such deposits are not observed when the inhibitor solution is used. X-ray microanalysis was used to obtain qualitative information about the chemical make up of these crystals. Figure 9 shows X-ray data obtained from one of the crystals from Figure 7B. A strong Cl line is observed at 2.640 keV. In addition, this crystals shows Cu lines at 0.960, 8.080 and 8.920 keV. Emission lines due to gold are also observed because of the Au that was sputtered onto the samples.

Figure 10 shows X-ray data obtained from the surface from Figure 8A; the Cl line is not observed. These data suggest that the crystals observed from the uninhibited surface are either CuCl or CuCl₂. However, quantification from the relative intensities of the Cu and Cl signals in Figure 9 gave superstoichiometric amounts of Cu (i.e., more moles of Cu than moles of Cl). This is undoubtedly because the X-ray data are obtained from both the crystals and the underlying Cu surface.

The kinetics and mechanism of the anodic dissolution of copper in HCl solution have been studied by many authors¹⁶⁻¹⁸. At concentrations less than 1M HCl the mechanism of dissolution is¹⁹



This mechanism would support the notion that these crystals on the surface of the uninhibited sample are CuCl. If this interpretation is correct, it would not be surprising that such crystals are not observed on the surface when inhibitor is added, because the inhibitor lowers the rate of corrosion. While this is in agreement with all of the electrochemical data, it is clear that chemical analysis of these crystals must be done before definitive conclusions can be made.

It is also of interest to consider the high magnification images shown in Figures 7A and 8A. The faceting seen in Figure 8A is a result of the differences in HNO₃-acid etch rates for the different crystal faces of copper²⁰. That this faceted surface is preserved after exposure to the HCl-plus-inhibitor solution

indicates that the Cu surface has not been significantly corroded by the HCl. This may be contrasted to the Cu surface obtained after exposure to HCl solution that contained no inhibitor (Figure 7A). Note that the faceting observed in Figure 8A is gone and that the surface is much more rough than when inhibitor is present. These images clearly show that corrosion is strongly inhibited when the best inhibitor is present in the HCl solution.

The results obtained here clearly show that adding a phenyl or p-tolyl group to the imidazole ring improves the ability of the molecule to inhibit Cu corrosion in 0.5M HCl solution. It is of interest to consider the mechanism of this inhibitory effect. Three possible mechanisms can be proposed - inhibition based on chemisorption^{3,7,12,21}, inhibition based on the formation of a Cu(II)-based polymer film^{20,22-26}, and inhibition based on physisorption. We will discuss each of these possibilities.

Chemisorption. Thierry and Leygraf have used surface-enhanced Raman spectroscopy to show that imidazole chemisorbs to Cu from 0.1 M aqueous NaCl solution²¹. Chemisorption has been proposed as a possible mechanism of corrosion inhibition for steel in 1 M H₂SO₄ solution³. However, it seems unlikely that chemisorption of imidazole and its derivatives would occur in acidic solutions such as 1 M H₂SO₄ or the 0.5 M HCl used here. This is because imidazole is a weak base and is present as the protonated, cationic form in such highly acidic solutions¹¹. Protonation decreases the number of lone pairs available for chemisorption from two to one, and would clearly lower the

basicity of the remaining lone pair. Finally, because Cu is d10, chemisorption (as opposed to physisorption, see below) involving simple donation of electron density from the imidazole to an empty d orbital on the metal seems impossible.²⁷ The only possibility would seem to be oxidative chemistry to form Cu(I) or Cu(II), followed by formation of a coordination complex between the inhibitor and the Cu ion. This possibility is discussed in next section.

Cu(II)-Based Films. It is well known that metallic Cu reacts with imidazole and its derivatives to form a polymeric film based on Cu(II) and the imidazolato ligand²². However, such films are typically prepared by applying imidazole to the metal surface and allowing the film-formation reaction to occur in air. The mechanism of film formation entails loss of the proton from the pyrrole nitrogen of the imidazole. Loss of this proton seems problematic in strongly acidic solution. Indeed, when such complexes are prepared from Cu²⁺ and imidazole, the solution must be strongly basic^{22,23}. In addition, in our best inhibitors (1-phenyl-4-methylimidazole and 1-(p-tolyl)-4-methylimidazole) the pyrrole proton is replaced by the phenyl or p-tolyl group. Therefore, if film formation does occur, the mechanism and stoichiometry would have to be very different than for films based on imidazole. Finally, the first step in the film formation process on Cu metal is chemisorption which is critical to the process because this increases the acidity of the pyrrole hydrogen^{22,26}.

Physisorption. Very early in corrosion research it was discovered that the extent of inhibition by the members of a homologous series of inhibitors increased with the molecular weight of the molecules in the series.²⁸

Hackerman showed, in studies with steel electrodes, that this is caused by an increase in physisorption of the higher molecular weight members of the homologous series of inhibitor molecules.²⁸ The results obtained here, that the higher molecular weight members of the imidazole series show better corrosion inhibition, are in agreement with this physisorption model for corrosion inhibition. Surface analytical data would be particularly helpful to explore the mechanism for these inhibitors.

CONCLUSIONS

The influence of methyl, hydroxymethyl, phenyl and tolyl substituents were studied.

- ◆ The value of z increases in the following order: hydroxymethyl < methyl < imidazole < phenyl < tolyl at optimum concentrations at temperatures ranging from 20 to 45 °C.
- ◆ AC impedance results at 20 °C are in good agreement with those obtained by potentiodynamic measurements for inhibition of copper corrosion in 0.5M HCl. These investigations have also shown that 1-(p-tolyl)-4-methylimidazole has the best inhibitory efficiency.

- ◆ Images obtained with SEM show the formation of crystalline deposits on the copper surface in 0.5M HCl and greater surface roughness. With the addition of 0.01M 1-(p-tolyl)-4-methylimidazole the surface roughness is considerably lower and facets are observed.
- ◆ Results obtained by X-ray microanalysis show that CuCl crystals are not formed with the addition of the best inhibitor to the 0.5M HCl solution.

ACKNOWLEDGMENTS

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List of Symbols

b_a, b_c Tafel coefficients (anodic and cathodic), mV

E_{corr} corrosion potential, mV

j_{corr} corrosion current density, mA cm^{-2}

R_p polarisation resistance, Ωcm^2

T temperature, $^{\circ}\text{C}$

Z electrode impedance, Ωcm^2

c concentration, mol dm^{-3}

f frequency, Hz

Greek letters

ω angular velocity, rad s^{-1}

Subscripts and superscripts

a anodic

c cathodic

corr corrosion

p polarisation

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TABLE 1. Corrosion parameters obtained via the Tafel-extrapolation method for copper in 0.5M HCl with and without the addition of the inhibitors at their optimum concentrations.

Temperature 20 °C					
Solution	E_{corr} mV	$-b_c$ mV d ⁻¹	b_a mV d ⁻¹	j_{corr} $\mu A cm^{-2}$	Z %
0.5 M HCl	-235.9	199.2	58.74	14.54	-
Inh 1	237.7	190.4	56.06	9.71	33.22
Inh 2	-248.8	190.8	58.05	10.66	26.69
Inh 3	-238.9	190.0	54.70	11.91	18.09
Inh 4	-256.9	191.4	67.75	8.92	38.65
Inh 5	-237.1	206.5	67.64	6.68	54.06
Temperature 30 °C					
0.5 M HCl	-234.9	220.2	62.80	28.80	-
Inh 1	-234.2	194.7	57.70	18.54	35.63
Inh 2	-243.0	202.1	61.50	18.67	35.17
Inh 3	-240.1	224.2	62.30	24.19	16.01
Inh 4	-246.6	207.3	65.14	18.42	36.04
Inh 5	-250.3	198.7	69.33	9.70	66.32
Temperature 35 °C					
0.5 M HCl	-236.5	219.3	60.30	31.84	-
Inh 1	-245.5	200.1	57.93	20.42	35.87
Inh 2	-244.0	187.0	56.30	22.37	29.74
Inh 3	-248.2	213.7	58.04	25.75	19.13
Inh 4	-251.3	200.6	61.89	20.34	36.12
Inh 5	-261.7	156.4	66.36	10.55	66.87
Temperature 45 °C					
0.5 M HCl	-225.6	240.0	66.20	43.79	-
Inh 1	-256.2	207.2	60.54	36.38	16.92
Inh 2	-253.6	201.3	60.00	37.00	15.51
Inh 3	-252.6	255.5	59.40	41.86	4.41
Inh 4	-258.2	216.0	65.36	31.39	28.32
Inh 5	-275.7	164.0	70.75	18.52	57.71

Inh 1 - imidazole, 0.1M

Inh 2 - 4-methylimidazole, 0.0005M

Inh 3 - 4-methyl-5-hydroxymethylimidazole, 0.1M

Inh 4 - 1-phenyl-4-methylimidazole, 0.005M

Inh 5 - 1-(p-tolyl)-4-methylimidazole, 0.1M

FIGURE CAPTIONS

Figure 1 The inhibitor compounds studied.

Figure 2 Anodic and cathodic Tafel lines for copper in 0.5M HCl without (1) and with the addition of 0.01M imidazole (2), 4-methylimidazole (3), 4-methyl-5-hydroxymethylimidazole (4), 4-methyl-1-phenylimidazole (5) and 1-(p-tolyl)-4-methylimidazole (6) at 30 °C.

Figure 3. Anodic and cathodic Tafel lines for copper in 0.5M HCl with the addition of 0.1M 1-(p-tolyl)-4-methylimidazole at 20 °C (1), 30 °C (2), 35 °C (3) and 45 °C (4).

Figure 4 Linear-polarisation curves for copper in uninhibited 0.5M HCl (1) and with the addition of 0.1M imidazole (2), 0.0005M 4-methylimidazole (3), 0.1M 4-methyl-5-hydroxymethylimidazole (4), 0.005M 4-methyl-1-phenylimidazole (5) and 0.1M 1-(p-tolyl)-4-methylimidazole (6) at 45 °C.

Figure 5. Linear-polarisation curves for copper in 0.5M HCl with the addition of 0.01M 1-phenyl-4-methylimidazole at 20 °C (1), 30 °C (2), 35 °C (3) and 45 °C (4).

Figure 6a) Nyquist plot for copper in 0.5M HCl without (●) and with the addition of 0.01M imidazole (□).

Figure 6b) Nyquist plot for copper in 0.5M HCl without (●) and with the addition of 0.01M 4-methylimidazole (▼) at 20 °C.

Figure 6c) Nyquist plot for copper in 0.5M HCl without (●) and with the addition of 0.1M 4-methyl-5-hydroxymethylimidazole (▲) at 20 °C.

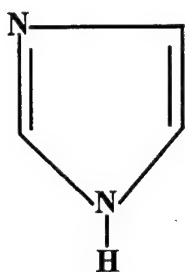
Figure 6d) Nyquist plot for copper in 0.5M HCl without (●) and with the addition of 0.01M 1-phenyl-4-methylimidazole (◆) and 0.01M 1-(p-tolyl)-4-methylimidazole (+) at 20 °C.

Figure 7 Scanning electron microscopic images of the surface of a copper sample after immersion for 12 hours in 0.5M HCl. Magnification 5000 (A) and 625 (B).

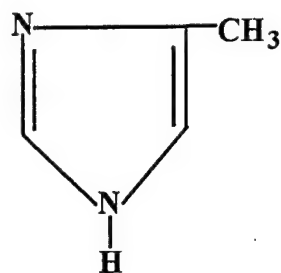
Figure 8 Scanning electron microscopic images of the surface of a copper sample after immersion for 12 hours in a solution 0.5M in HCl and 0.01M in 1-(p-tolyl)-4-methylimidazole. Magnification 5000 (A) and 625 (B). X-ray microanalysis shows that the small bright white spots are Au from the sputtered Au film.

Figure 9 X-Ray microanalysis of a copper sample exposed to 0.5M HCl for 12 hours.

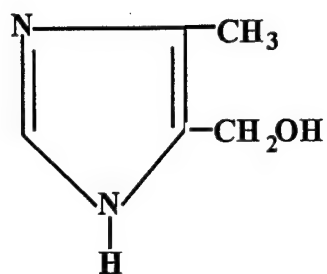
Figure 10 X-Ray microanalysis of a copper sample exposed to 0.5M HCl plus 0.01M 1-(p-tolyl)-4-methylimidazole for 12 hours.



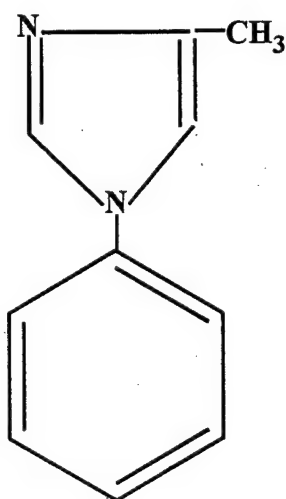
imidazole



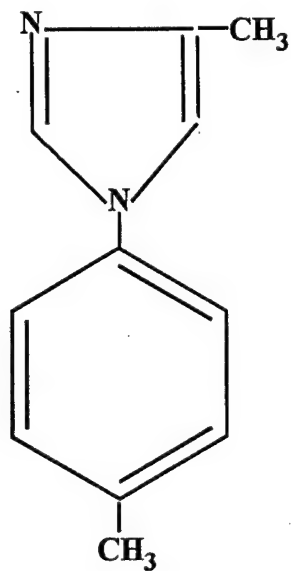
4-methylimidazole



4-methyl-5 hydroxymethylimidazole



1-phenyl-4-methylimidazole



1-(p-tolyl)-4-methylimidazole

